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Dioxaphosphorinane chair to half-chair conversion caused by cis- to trans-enol transformation of the β-ketoester substituent

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Abstract

The X-ray single crystal structure 5,5-dimethyl-2-(methoxycarbonyl-3′-oxo-2′-butyl)-2-oxo-1,3,2-dioxaphosphorinane (**I**) reveals an unusual half-chair conformation of the dioxaphosphorinane substituent on a trans-enol ring. NMR and IR solution data provide support that the same structure displays a strong conformational preference while the minor forms are chair conformers with an axial and equatorial cis-enol ring.

1. Introduction

Hydrogen bonds play an essential role in the stabilisation of the conformations of molecules [1–4]. Intermolecular hydrogen bonding influences the formation of boat and chair conformations of five-coordinated phosphorinane in the model compounds for the reactions of cyclic adenosine 3′,5′-monophosphate, c-AMP [5]. This was considered as evidence of the low-energy difference, within the scale of hydrogen bonding energy, for boat, twist-boat, twist-chair and chair conformations for the phosphorinane molecules. On the contrary, the half-chair conformation is relatively rare for the phosphorinane ring, being obviously of highest energy. This intriguing conformation was twice predicted for the equatorial/equatorial 3′,5′-dioxaphosphorinane ring [6,7], but the only known experimental evidence has been reported for *cis*-4,6-dimethyl-2-oxo-2-triphenylmethyl-1,3,2-dioxaphosphorinane due to forced intramolecular van der Waals contacts [8]. The formation of intermolecular hydrogen bonding has little effect on the conformation of the four-coordinated 1,3,2-dioxaphosphorinane ring, which adopts a chair conformation [9–11].

In a related study of the 2-oxo-1,3,2-dioxaphosphorinane derivatives of cis-enolized pentane-2,4-diones [12–14], we reported recently that the phosphorinane ring adopts a chair conformation when the enol substituent is attached to the phosphorinane ring in either an axial or an equatorial position. Open-chain β-ketocarboxylic esters, existing in the trans configuration of the enol

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